

## A Simple Method to Produce Trivalent Colloidal Particles

Shan Jiang and Steve Granick\*

Departments of Materials Science and Engineering, Chemistry, and Physics, University of Illinois,  
Urbana, Illinois 61801

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Trivalent patchy colloidal particles are synthesized using a two-step  $\mu$ -contact printing method. First, one pole of a particle is modified, then the other. With the center portion of the particle left intact, the final chemical makeup consists of three distinct patches of different chemical composition whose relative areas can be controlled. This method depends on preparing stamps with sufficient adhesion to lift off particles yet mild enough adhesion for their subsequent detachment. Furthermore, this method adjusts stamp stiffness, allowing the respective areas of the two printed poles to be controlled separately. To check the efficacy of the method, the shapes of the chemically modified poles were examined using scanning electron microscopy (SEM) after Au nanoparticle adsorption. Fluorescence imaging further confirmed the trivalent patchy particle geometry.

## Introduction

Experimentalists are racing to catch up with modeling and computer simulations,<sup>1–3</sup> which show that particles with anisotropic chemical makeup can assemble into interesting structures distinctly different from those taken by particles whose chemical makeup is homogeneous. Structures suggested by those studies have the potential to enable much new functionality, including environmentally responsive shapes,<sup>4</sup> photonic materials,<sup>5</sup> novel mechanical properties,<sup>6</sup> and assemblies whose directional interactions would be analogous to the chemical reactions between molecules, although the nature of the linking bond is envisaged to be physical interactions rather than the conventional covalent bond. However, progress on the experimental side has been held back by the paucity of synthetic methods capable of producing monodisperse samples in the laboratory.

Routes to produce the needed elementary particles have been dominated by methods to produce the simplest possible form of anisotropic chemical makeup, the Janus particle whose surface is divided into just two different chemical compositions. There are now many synthetic strategies to this end, which have been reviewed recently.<sup>7</sup> Methods to fabricate Janus particles in large quantity have been developed.<sup>8–10</sup> On the other hand, more

complex structures have been formed by linking magnetic colloids,<sup>11</sup> by external electric fields,<sup>12</sup> by electrified jetting,<sup>13</sup> by glancing angle metal deposition,<sup>14</sup> and by stamping.<sup>15,16</sup> Here we report a simple, efficient method to synthesize trivalent patchy particles, which are more complex than the traditional Janus geometry. We go beyond presenting the synthetic approach and characterize the resulting trivalent structure. Compared with the traditional  $\mu$ -contact printing method, the new method is advantageous in terms of simpler procedure and better control of geometry. We demonstrate not only the simplicity of the approach but also fidelity of formation and show that the resulting structures are well-defined and monodisperse.

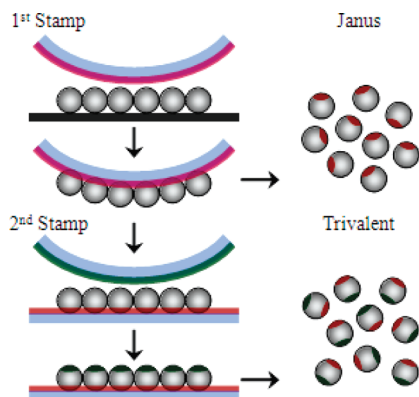
As demonstrated in Figure 1, the idea is to start with monodisperse particles whose shape is already definite and to modify their surface chemical makeup using  $\mu$ -contact printing first on one side, then on the other. The difficulty with traditional application of this approach is first that an adhesion layer must be applied between the particle and the substrate,<sup>17</sup> which greatly limits the size and the geometry of the Janus particles that can be synthesized. A second limitation is that a cleaning step is needed, after printing, to remove the adhesion layer. Furthermore, reliance on printing surfactant molecules limits the possible chemical makeup.<sup>18</sup> The method introduced here simplifies the process by overcoming these limitations.

One starts with a monolayer of colloidal particles on a flat substrate. These are made of silica in the examples shown below, but the method applies generally. A monolayer of silica particles is easily formed by evaporating an aqueous suspension of these particles, the resulting spots of multilayer buildup being removed naturally by the process itself as described below. The polydimethylsiloxane (PDMS) stamp was prepared by mixing Sylgard 184 agents. Immediately before stamping, the PDMS surface was treated by oxygen plasma to provide needed adhesion to the particles as well as wettability. In the implementation described

\*Corresponding author.

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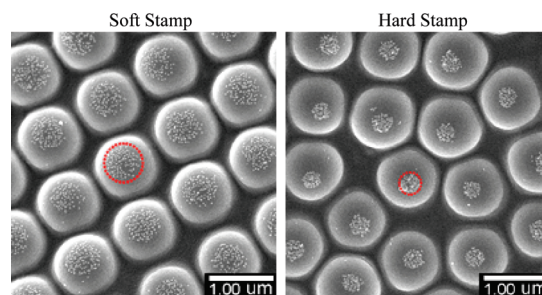
**Figure 1.** Scheme to form trivalent patchy colloidal particles. A first PDMS stamp lifts outermost particles from the surface after they have been deposited as a monolayer or multilayer onto a solid support. A second PDMS stamp does the same to the opposing pole of these particles. The central unmodified surface area comprises a region of third chemical makeup. Finally, trivalent particles are released.

here, silane solution was spread onto the PDMS stamp by spin coating. The stamp was then brought into contact with the silica particle monolayer. Mechanical pressure was applied to ensure conformal contact. When the stamp was separated from the substrate after 30 min, particles adhered to the stamp and were lifted off together with it. The excess silane on the stamp was rinsed away by ethanol. This process results in chemical modification of one pole of the particles, a pole that is now protected by its adhesion to the stamp; the opposite pole is now open to being subsequently stamped in a second step, and this second stamping step is simple to carry out. As the two print processes are completely separate, different chemicals can be applied. Finally, the particles are released by ultrasonication.

In this method, adhesion is provided by the PDMS stamp itself; no separate adhesion layer such as a gel is needed, although this is the traditional approach.<sup>17,18</sup> Nor is it necessary to begin with a well-formed colloidal monolayer, as particles are lifted off the original surface by printing, with those particles without good contact with the stamp being left on the substrate and discarded. In this way, modified and unmodified particles are separated automatically; those particles that are successfully lifted up are guaranteed to be modified chemically at their pole. Key to the success of this method is to begin with appropriate plasma treatment of the PDMS stamp. There have been reports that adhesion to a stamp depends on plasma power, chamber pressure, and treatment duration.<sup>19</sup> Whichever specific condition is selected for implementation, the requirement is that adhesion must be strong enough to lift particles off the substrate when the stamp is detached, but not so strong that the particles cannot subsequently be released by ultrasonication. By optimizing the parameter of the plasma treatment, more than 80% of the particles on the substrate can be lifted up by the PDMS stamp.

### Experimental Section

**Chemicals.** Silica particles 1  $\mu\text{m}$  in diameter were purchased from Tokuyama, Japan, and used without further treatment. Silica particles 150 nm in diameter were synthesized using a



**Figure 2.** SEM images of 1  $\mu\text{m}$  silica particles with one pole stamped with amino silane, and then image contrast was introduced by allowing Au nanocrystals to adsorb to the silane-modified region. This area of chemical modification is highlighted by a red circle. The top panel shows that using a soft PDMS stamp yields a large ( $\sim 520$  nm) diameter of chemically modified area; the bottom panel shows that, when using a harder stamp but the same printing pressure, the diameter of the chemically modified area is nearly half this level,  $\sim 300$  nm. The size of the chemically modified area can be adjusted with high fidelity by adjusting the stiffness of the PDMS stamp. For a soft stamp, the monomer-to-cross-linking agent ratio is 10:1; while for hard stamp the ratio is 2:1.

modified Stöber method.<sup>20</sup> *N*-(6-Aminohexyl) aminopropyltrimethoxysilane (95%) was purchased from Gelest and used without further purification.

Au nanoparticles were prepared by the method reported by Frens.<sup>21</sup> Typically, 10 mL of 1% (w/v) sodium citrate solution is added into a boiling solution of 290 mL of 0.015% (w/v)  $\text{HAuCl}_4$ . Within 3 min, the clear solution changes to a wine-red color, which indicates the formation of Au nanoparticles. After further boiling for 10 min, the heat source is removed, and the dispersion is cooled to room temperature. Reducing the volume of sodium citrate solution to 4.3 mL leads to 28 nm Au nanoparticles.

**Printing Procedure.** The printing procedure was adapted from a method developed by others previously for printing on a flat silica substrate.<sup>22</sup> First, a monolayer of silica particle was formed by simple evaporation of 1  $\mu\text{m}$  silica particle aqueous solution (2 wt %) on a flat substrate. For 150 nm silica particles, multilayers will build up on the substrate, but the method still applies. PDMS stamps were prepared by mixing Sylgard 184 agents. Stamps of different stiffness were produced by mixing different ratios of the monomer and the cross-linking agent. Just before stamping, the PDMS surface was treated by oxygen plasma to induce necessary adhesion and wettability. The oxygen plasma was generated by a Harrick PDC-32G plasma cleaner. In a typical experiment, low plasma power was used (6.8 W), and the chamber pressure was  $\sim 150$  mTorr. The treatment duration was 50 s. The printing was carried out immediately after the plasma treatment. *N*-(6-aminohexyl) aminopropyltrimethoxysilane was selected to bond amine groups onto the silica particle surface, as the amine group provides an easy site for further chemical modification, such as dye labeling. Rhodamine B and fluorescein (Aldrich-Sigma) were attached to the silane using a procedure described in the literature.<sup>23</sup> In a typical experiment, 50  $\mu\text{L}$  of silane-dye solution of 1 mM was spread onto the PDMS stamp by spin coating at 3000 rpm for 30 s. The stamp was then brought into contact with the silica particle monolayer. Pressure ( $\sim 3 \times 10^4$  Pa) was applied to ensure conformal contact. After 30 min, the stamp was separated from the substrate, particles adhering to the stamp. Excess silane-dye solution on the stamp was rinsed off using ethanol. The same stamping process was then applied to modify the other side of the particles. Since the two stamping processes are completely distinct, different chemicals can be applied to

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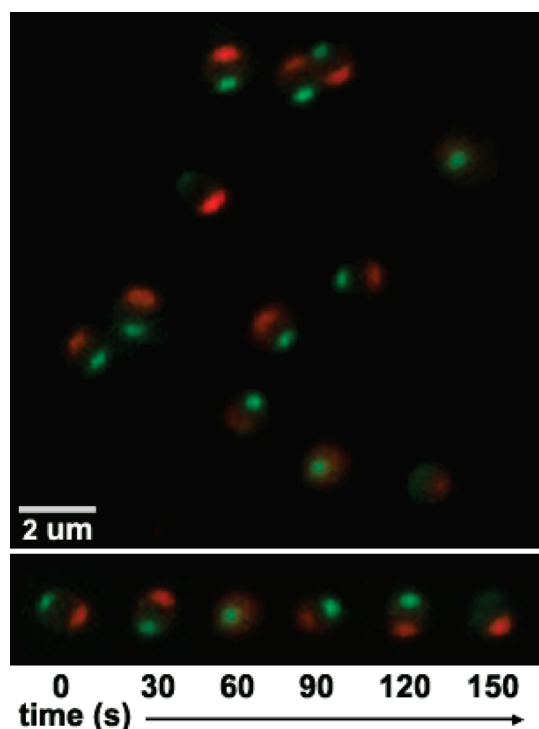
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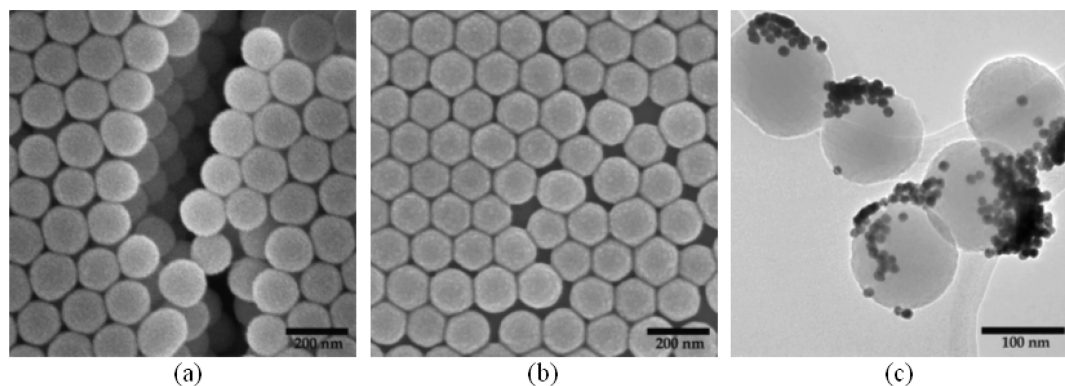
modify the silica surface. Finally, the trivalent particles can be released by ultrasonication in ethanol for 30 min. Possible spreading of inks across the surfaces of silica beads was not noticed to be problematic. The yield was determined by the area of physical contact with the stamp.

### Results and Discussion

In this field of study, a limitation has been the difficulty to characterize the fidelity with which anisotropic surface chemistry is imparted to particles. The selective adsorption of Au nanocrystals to one chemical area affords a way to visualize the resulting anisotropy with submicrometer resolution by scanning



**Figure 3.** Epifluorescence images of trivalent colloidal particles with red dye attached to one pole and green dye attached to the other pole. The top panel is a snapshot of the field of view, showing particles in aqueous/glycerol suspension with random orientations. The bottom panel, displaying images of the same particle at different times, shows reorientation dynamics in real time and the potential to visualize the orientation of trivalent particles when they assemble into clusters.



**Figure 4.** SEM and TEM images of silica particles 150 nm in diameter. (a) Multilayers of particles deposited on a wafer before printing. (b) Monolayer of particles on a PDMS stamp after printing; beneath the particles is the PDMS stamp. (c) TEM image of Janus particles labeled with Au nanocrystals.

electron microscopy (SEM). Implementing this approach, we allowed Au nanocrystals (20 nm) to adsorb onto patches printed with a silane terminated with an amine group. The SEM images in Figure 2 illustrate that the area of the surface chemical modification is nearly the same for each particle. A key point is that, simply by changing the softness of the PDMS stamp (by mixing the Sylgard 184 curing agents at different ratios), under the same stamping pressure, the modified area can be purposefully controlled. As also illustrated in Figure 2, the softer the PDMS stamp, the larger the area of chemical modification. This control over surface area presents another advantage of the method described here.

Going beyond SEM images in the dry state, fluorescence microscopy was used to visualize the trivalent structure of particles in aqueous suspension. To this end, rhodamine B (red) and fluorescein (green) were printed onto opposite poles of silica particles. Fluorescence from the two poles is easily distinguished, the unlabeled central portion appearing dark. By adding glycerol (90%) to slow down diffusion, Brownian rotation of the particles was observed as shown in Figure 3.

An additional advantage of this method is its capability to modify even smaller colloidal particles, although particles smaller than 500 nm in diameter are too small to allow discriminating opposite poles, as done here in Figure 3. Using traditional methods, this would be difficult, reflecting the difficulty of forming well-ordered monolayers to begin with, when colloidal particles are so small. However, the method presented here does not require starting with a well-formed monolayer as during the printing process; only the outermost particles are lifted off. We find that this method works with particles as small as 150 nm in diameter. Multilayers were built up on the substrate during the evaporation of the particle solution as shown in Figure 4a. This is problematic in the traditional method to make Janus particles by metal deposition, as particles below the outermost layer are shielded from coating, but presents no problem using this new method, as the PDMS stamp will pick up at most one monolayer of particles, as shown in Figure 4b. Figure 4c shows a transmission electron microscope (TEM) image of Janus particles made from 150 nm silica particles.

This method to synthesize trivalent patchy particles is simple and produces products of high purity with good fidelity. The versatility of silane coupling allows one to deposit a large variety of potential functional groups onto the surfaces of colloidal particles, not just those illustrated here. Although demonstrated here for spheres, the method should apply just as

well to other elemental shapes such as cubes, ellipsoids, and so forth. Looking for uses of trivalent particles, we envision many possibilities.

If the central portion is hydrophobic and the poles are polar, we envision that sheets will form spontaneously. If the two poles are attractive to one another, we envision that linear chains will form spontaneously; there are also possibilities to form network structures by mixing particles of different functionality and different size. The potential structures that will form spontaneously from the assembly of these trivalent

patchy particles augment the known structures formed by divalent (Janus) particles.

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